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Destruction of Air Emissions Using Catalytic Oxidation

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by

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Incinerators	Stripping	Stationary Sources		07A, 13H
Catalysis	Graphic Arts	Catalytic Oxidation	07D	14E, 05F
Organic Compounds		Groundwater Stripping	07C	
Volatility	Flexography	Heatset Printing	20M	
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DESTRUCTION OF AIR EMISSIONS USING CATALYTIC OXIDATION

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ABSTRACT

Catalytic incineration is an air pollution control technique in which volatile organic compounds (VOCs) and vapor-phase air toxics in an air emission stream are oxidized with the help of a catalyst. Design of catalytic systems for control of point source emissions is based on stream-specific characteristics and desired control efficiency. This paper discusses the key emission stream characteristics and hazardous air pollutant (HAP) characteristics that affect the applicability of catalytic oxidation.

The application of catalytic oxidation technology to four types of air emission sources is discussed. These are: (1) groundwater stripping operations; (2) graphic arts facilities; (3) flexographic printing plants; and (4) latex monomer production. The characteristics of each of these emissions are discussed along with the catalytic technology used to control these emissions.

In addition, several catalytic systems for control of air emissions are identified along with information about their technology and their position in the market place. Finally, some rough economics are presented which compare catalytic oxidation, carbon adsorption, and thermal incineration systems.

INTRODUCTION

The most frequent approach to point source air emissions control is the application of add-on control devices. For organic vapors, these devices can be of two types: combustion and recovery. Applicable combustion devices are thermal incinerators, catalytic incinerators, flares, and boilers/process heaters. Applicable recovery devices include condensers, adsorbers, and absorbers. The combustion devices are the more commonly applied control devices, since they are capable of high removal (i.e., destruction) efficiencies for almost any type of hazardous air pollutant (HAP). The removal efficiencies of the recovery techniques generally depend on the physical and chemical characteristics of the HAP under consideration.

Applicability of the control techniques depends more on the individual emission stream under consideration than on the particular source category (e.g., degreasing vs. surface coating in the solvent usage operations source category). Thus, applicable control techniques for point source emissions are selected on the basis of stream-specific characteristics and desired control efficiency. The key emission stream characteristics and HAP characteristics that affect the applicability of each control technique are: HAP/organics content, heat content, moisture content, flow rate, temperature, and molecular weight.

Matching the characteristics of the stream under consideration with the useful ranges of the control devices will help the user to identify those techniques that can potentially be used to control the emission stream. Catalytic oxidation, for example, is generally useful for concentrations of 50 to 10,000 ppmv, if the total concentration is less than 25% of the lower explosive limit (LEL), and for flow rates of less than 100,000 scfm (170,000 Nm^3/hr). The list of potential applicable control techniques can then be narrowed further depending on the capability of the applicable control devices to achieve the required performance levels. For example, catalytic incineration can achieve an expected control efficiency of greater than 95% at total volatile organic compound (VOC) concentrations of greater than 100 ppmv. Very little data regarding control device removal efficiency for specific HAPs are available. Therefore, without actual source test data for a specific emission stream and control system, HAP removal efficiency is generally assumed to equal total VOC removal efficiency (1).

CATALYTIC OXIDATION TECHNOLOGY

The topic of this presentation is catalytic incineration, which is also called catalytic oxidation and catalytic destruction. Catalytic incineration

is an air pollution control technique whereby VOCs and vapor-phase organic air toxics in an air emission stream are oxidized with the help of a catalyst. A catalyst is a substance that accelerates the rate of a reaction at a given temperature without being appreciably changed during the reaction. Catalysts typically used for VOC incineration include platinum and palladium. Other formulations are also used, including metal oxides for emissions streams containing chlorinated compounds.

A typical catalytic oxidation system with primary and secondary heat recovery is shown in Figure 1. Process air emissions, generally at ambient temperatures, are passed though the primary heat exchanger to recover heat from hot exhaust gases. If necessary, the emission stream is then preheated to catalytic oxidation temperatures in a natural-gas-fired, or electric preheater before passing into the catalyst bed. A small portion of the process air emissions is separated from the controlled stream and used as combustion air before primary heat exchange.

The catalyst bed (or matrix) is generally a metal-mesh-mat, ceramic honeycomb, or other ceramic matrix structure designed to maximize catalyst surface area. Catalysts may also be in the form of spheres or pellets which may operate either in a fixed or fluidized bed configuration. Care must be taken that high preheat temperatures accompanied by the increase in temperature due to combustion do not result in high operating temperatures in the catalyst bed. This could cause the catalyst bed to overheat and eventually lose its activity.

Exhaust gases then pass through the hot side of the primary heat exchanger, giving up heat to the inlet stream. If the economics are favorable, secondary heat recovery is used. Recovered heat is often used for process heat or, in the case of printing operations, for dryer makeup air preheating. If the oxidized streams contain chlorinated compounds, caustic scrubbing may be required before the exhaust stream can be emitted to the atmosphere.

The performance of a catalytic incinerator is affected by several factors including: (a) operating temperature, (b) space velocity (reciprocal of residence time), (c) VOC composition and concentration, (d) catalyst properties, and (e) presence of poisons/inhibitors in the emission stream. In catalytic incinerator design, the important variables are the operating temperature at the catalyst bed inlet and the space velocity. The operating temperature for a particular destruction efficiency is dependent on the concentration and composition of the VOC in the emission stream and the type of catalyst used.

Space velocity is defined as the volumetric flow rate of the combined gas stream (i.e., emission stream + supplemental fuel + combustion air) entering the catalyst bed divided by the volume of the catalyst bed. As such, space velocity also depends on the type of catalyst used. At a given space velocity, increasing the operating temperature at the inlet of the catalyst bed increases the destruction efficiency. At a given operating temperature, as space velocity is decreased (i.e., as residence time in the

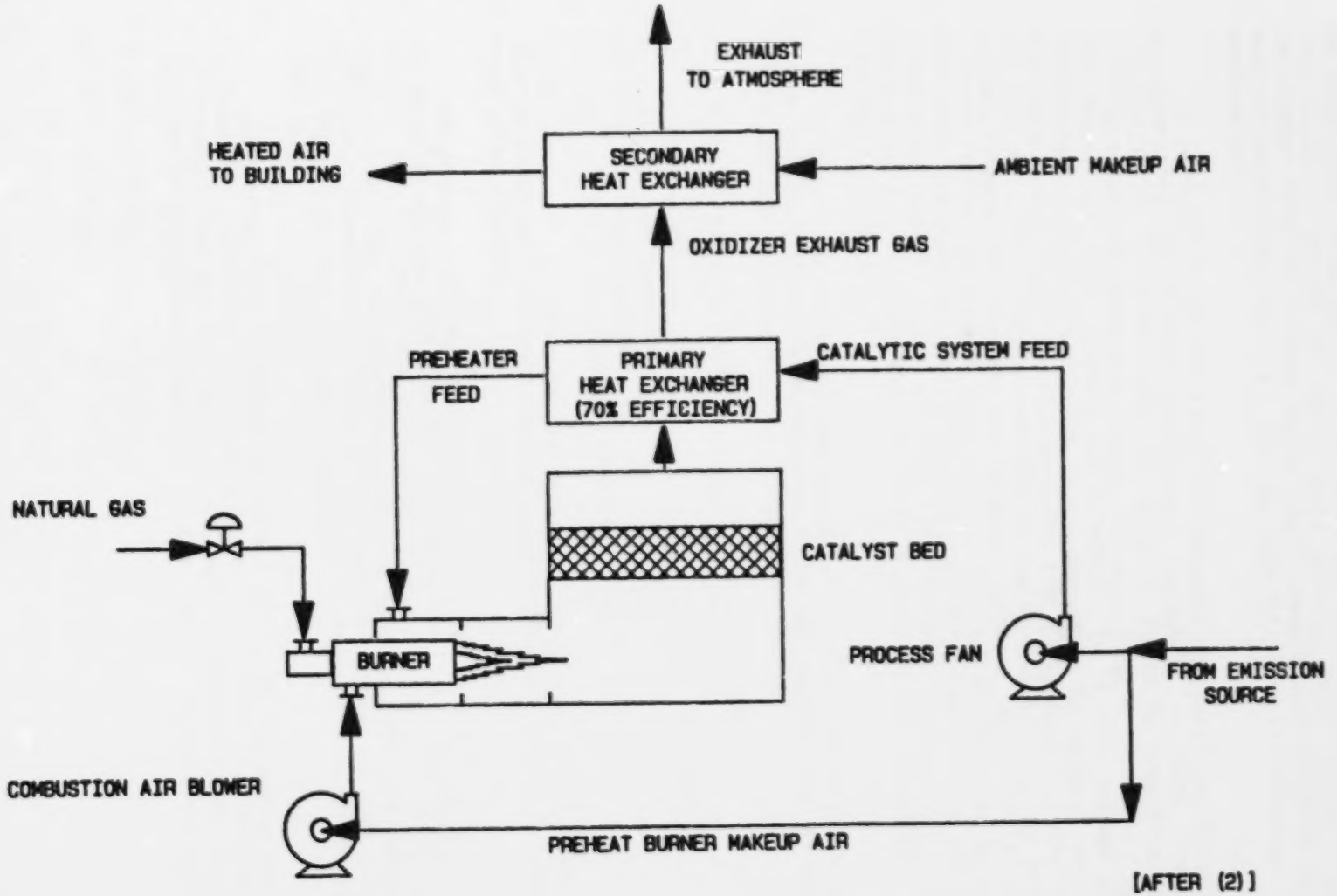


Figure 1. Process flow sketch - catalytic oxidation system.

catalyst bed increases), destruction efficiency increases. Catalytic incinerators can achieve overall VOC destruction efficiencies up to about 98% and HAP destruction efficiencies up to about 95% with space velocities in the range 30,000 to 100,000 gas hourly space velocity (GHSV) (3,4,5). However, the greater catalyst volumes and/or higher temperatures required for high destruction efficiencies (i.e., 99%) may make catalytic incineration uneconomical.

The performance of catalytic incinerators is sensitive to pollutant characteristics and process conditions. Therefore, in these introductory discussions, it is assumed that the emission stream is free from poisons/inhibitors such as phosphorus, lead, bismuth, arsenic, antimony, mercury, iron oxide, tin, zinc, sulfur, and halogens. It is also assumed that the fluctuations in process conditions (e.g., changes in VOC content) are kept to a minimum as are liquid or solid particles that could deposit on the catalyst and form a coating, thereby reducing the catalyst's activity by preventing contact between the VOCs and the catalyst surface. Additionally, catalyst life is limited by thermal aging and by loss of active sites by erosion, attrition, and vaporization. With proper operating temperatures and adequate temperature control, these processes are normally slow, and satisfactory performance can be maintained for 3 to 5 years before replacement of the catalyst is necessary.

The data necessary to perform design calculations consist of the emission stream characteristics listed below and of the HAP control level as determined by the applicable regulations (1). These data are:

- Maximum Flow Rate [scfm (Nm^3/hr)]
- Temperature [°F (°C)]
- Heat Content [Btu/scf (kcal/Nm^3)]
- Oxygen Content (%)
- Moisture Content (%)
- Required Destruction Efficiency (%)

If dilution air is added to the emission stream upon exiting the process, the data that will be used in the calculations are the resulting characteristics after dilution.

In general, catalytic incineration is applied to dilute emission streams. If emission streams with high VOC concentrations [i.e., heat content above 10 Btu/scf (89 kcal/Nm^3) for air + VOC mixtures] are treated by catalytic incineration, they may generate enough heat upon combustion to deactivate the catalyst. Therefore, dilution of the emission stream to heat contents of less than 10 Btu/scf with air is necessary to reduce the concentration of the VOCs (1).

Table 1 presents suggested values and limits for the design variables of a fixed bed catalytic incinerator system to achieve a given destruction efficiency. For specific applications, other temperatures and space velocities may be appropriate depending on the type of catalyst employed and the

emission stream characteristics (i.e., composition and concentration). For example, the temperature of the flue gas leaving the catalyst bed may be lower than 1,000 °F (538 °C) for emission streams containing easily oxidized compounds and still achieve the desired destruction efficiency. Note that the destruction efficiency for a given compound may vary depending on whether the compound is the only VOC in the emission stream, or it is part of a mixture of VOCs (3).

Table 1. Catalytic Incineration System Design Variables (4,5,6)

Required destruction efficiency (%)	Minimum temperature at the catalyst bed inlet [°F(°C)]	Temperature at the catalyst bed outlet (Minimum-Maximum) [°F(°C)]	Space velocity (hr^{-1})
90	600 (316)	1,000-1,200 (538-649)	40,000
95	600 (316)	1,000-1,200 (538-649)	30,000

Supplementary fuel is added to the catalytic incinerator system to provide the heat necessary to bring the emission stream up to the required catalytic oxidation temperature for the desired level of destruction efficiency. For a given inlet temperature, the quantity of supplementary heat needed is provided by: (a) the heat supplied from the combustion of supplementary fuel, (b) the sensible heat contained in the emission stream as it enters the catalytic incinerator system, and (c) the sensible heat gained by the emission stream through heat exchange with hot flue gases. If recuperative heat exchange is not practiced at a facility, then item (c) will be zero.

CASE STUDY 1: AIR STRIPPING OF GROUNDWATER

Air stripping of groundwater has been shown to be an efficient and cost effective method of removing VOCs from groundwater and soil. The removal of dissolved fuel fractions and chlorinated solvents at efficiencies in excess of 95% has been demonstrated on several occasions. Unfortunately, these contaminants are transferred to the air where they may continue to pose an environmental and health threat. Regulation of such emissions has already been considered in many states including Michigan and California.

The applicability of catalytic oxidation to the control of groundwater

stripping gaseous emissions will be reviewed with special attention given to system designs and case histories. The variety of contaminants and catalyst poisons encountered in stripping operations will also be reviewed. Presently, few options are available for the control of groundwater air stripping emissions. Vapor-phase carbon adsorption and thermal incineration are the two treatment methods which are best established. These technologies have some disadvantages. Adsorption merely transfers the contaminant to a solid phase, which in turn requires disposal or regeneration. Regeneration with steam results in a contaminated waste water stream which requires treatment and disposal. Thermal incineration may be expensive, since it requires a substantial energy input to destroy dilute gas-phase contaminants. Catalytic oxidation is establishing itself as a new alternative to these more established technologies. Like thermal incineration, it is an ultimate disposal method, but since it operates at much lower temperatures, the energy costs are also lower.

A hypothetical system with catalytic destruction of air stripping effluents is pictured in Figure 2 (7). Air is countercurrently contacted with a contaminated water stream. Most volatile compounds are transferred to the air stream, and the water receives a final cleanup in the liquid polishing step before disposal. The catalytic destruction of organic emissions in the air stream differs from other catalytic pollution control applications in several important aspects. First, the concentration of the contaminants in the gas phase is quite low, in most cases less than 100 ppmv. Second, the humidity levels are unusually high since the air stream is saturated coming off the stripping unit. Third, a wide variety of contaminants and mixtures ranging from chlorinated compounds and soluble fuel fractions to pesticides and polychlorinated biphenyls may be in any groundwater source. Finally, the air stream exiting a groundwater stripper may have high concentrations of mineral aerosols and catalyst poisons (e.g., hydrogen sulfide) that will shorten catalyst life. All of these factors make the design and implementation of catalytic treatment uncertain.

The emissions from air stripping units may consist of a complex mixture of reactants including both fuel and solvent fractions. A typical example of an air stripping off gas stream is shown in Table 2. This table lists the concentration of selected contaminants emitted from a pilot air stripping unit at Wurtsmith Air Force Base in Michigan (8). Here, no individual contaminant exceeds 70 ppmv, but the cumulative total exceeds 170 ppmv.

The energy burden of heating a cold, water-laden air stripping effluent stream should be lower for a catalyst system than for thermal incineration, but it still represents a considerable operating cost. The air from most air stripping units can be considered to be saturated with water (100% relative humidity). This corresponds to an absolute water vapor concentration of between 0.8 and 3.1% in the exit stream. The action of bubbles in the stripping unit also produces a large amount of liquid aerosol. The carryover of liquid water in the form of small droplets and aerosol represents an additional large heat burden on any catalyst bed and should be minimized by the use of demisters or filters if possible. Aerosol removal has an additional

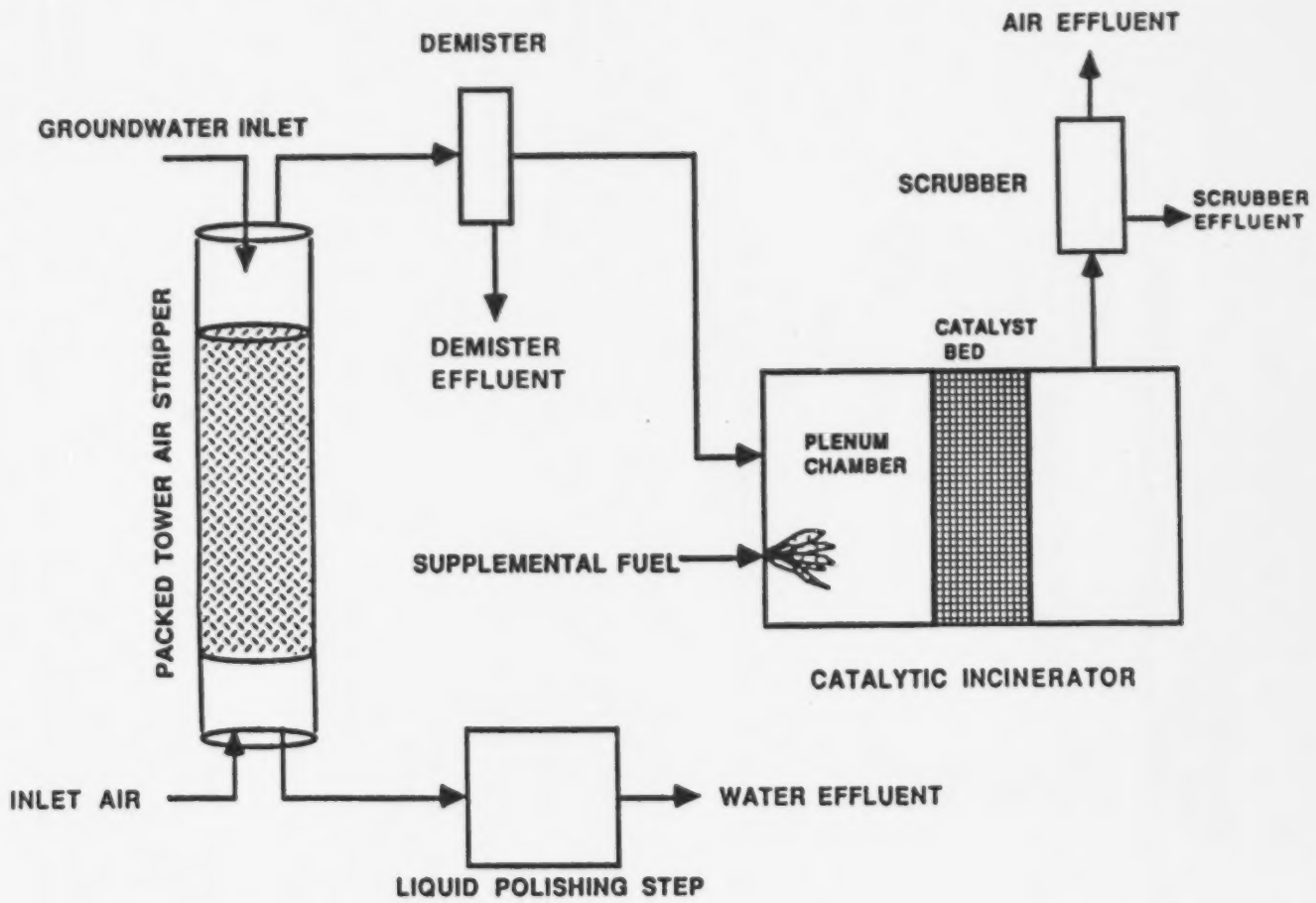


Figure 2. System configuration for catalytic destruction of air stripping emissions.

advantage, in that mineral or biological matter which might foul and deactivate the catalyst bed is also removed.

Table 2. Typical Organic Concentrations in Air Stripping Overhead (8)

Compound	Concentration in gas phase (ppmv)[a]
Pentane	42.4
Cyclohexane	66.1
Methyl cyclopentane	7.7
2,3-Dimethyl butane	1.6
Trichloroethylene	17.9
Benzene	9.2
Ethyl benzene	8.3
Cumene	3.4
Mixed xylenes	21.3
Total	177.9

[a]Calculated at a gas/liquid ratio of 42/1 for 1-in. (2.5-cm) Pall rings.

The high concentration of water vapor in the emission stream represents a major difference between this application of catalytic control and other more typical applications. As of now, no firm basis exists to predict the behavior of non-halogenated hydrocarbon oxidation in the presence of water. On the other hand, the effect of water on the catalytic destruction of chlorinated compounds is generally thought to be beneficial. The most easily treated products of this process are hydrochloric acid (HCl), carbon dioxide, and water; however, some solvents such as trichloroethylene (C_2HCl_3 do not have stoichiometric amounts of hydrogen to allow complete reaction of the chlorine to HCl. For those compounds, water may serve as this hydrogen source, or may merely favorably alter the reaction thermodynamics. Other hydrogen sources such as methane or propane may also be beneficial in promoting HCl formation. As with the non-halogenated hydrocarbons, a clearer understanding of the catalytic chemistry is essential to understanding the role of water vapor.

As a further complication, many contaminated groundwater sources may contain mixtures of hydrocarbons and halogenated compounds. Laboratory and pilot studies have found significant mixture effects for oxidation of hydrocarbons, chiefly in the form of inhibition (9,10). This means that the catalytic oxidation of a given compound is generally negatively impacted by the presence of mixtures, and higher catalyst bed operating temperatures may be necessary to achieve adequate destruction. Information on mixture effects for halogenated compounds is extremely limited.

Catalysts exposed to the air stripping effluent are subject to deactivation from several sources: fouling, thermal degradation, poisoning, and catalyst volatilization. The catalyst bed may plug or become encrusted, thereby losing its effectiveness due to dissolved salts and mineral matter in the air stripping off gases. As mentioned previously, removal of aerosols prior to the catalyst unit may alleviate this problem. If the catalyst bed is operated at high temperatures [greater than 1,110 °F (600 °C)] for prolonged periods, sintering of active noble metals may occur also resulting in loss of activity. Groundwater also often contains significant amounts of readily strippable compounds, such as hydrogen sulfide (H_2S), that may poison the catalyst surface by adsorbing and blocking active sites. Higher operating temperatures may remove some of these poisons, but sintering may then become a problem. Finally, some reactants, especially halogenated compounds, may chemically bond with the active catalyst and subsequently volatilize from the surface. The loss of catalyst associated with this vaporization process inevitably results in lower catalyst efficiency.

A recent EPA report (11) identified 177 air strippers in the United States. Of these, 17 are equipped with air emission controls. Of the 17 facilities, 1 uses a catalytic incinerator, 2 have open flares, 2 have thermal incinerators, and 12 have granular activated carbon adsorbers. Installation of the air control device was required by the governing state at 9 of these 17 sites.

The catalytic incinerator identified in Reference 11 is located at the U.S. Coast Guard Base in Traverse City, Michigan. This air stripper system began operation in 1985. The catalytic incinerator was included in the initial design and installation of the air stripping system. The air stripper installed at this site is a rotary high-gravity air stripper which achieves high removal efficiencies at lower air to water ratios than packed towers. The lower air flow for this type of air stripper results in higher pollutant concentrations in the air stripper exhaust. The catalytic incinerator at Traverse City was installed for destruction of benzene, toluene, and xylene stripped from the groundwater. The catalytic oxidation unit is designed for a flow of 2,000 scfm (3,400 Nm^3/hr) and operates at 500 to 600 °F (260 to 320 °C). The design efficiency for this catalytic incinerator was 90% (11). However, no performance data are available (12). The estimated installed cost for the catalytic unit is $198,500, and annual operating costs for the 2,000 scfm (3,400 Nm^3/hr) unit are $95,920 (based on third quarter 1986 data) (11).

A catalytic incinerator has been built for control of organic air emissions from air stripping of groundwater in two additional cases. The U.S. Air Force has installed a fluidized bed, nonprecious metal catalyst system for control of trichloroethylene and 1,2 dichloroethylene air stripping emissions at Wurtsmith Air Force Base in Michigan. The treated air flow is 1,100 scfm (1,870 Nm^3/hr) at an operating temperature of 900 °F (480 °C). Without auxiliary equipment, it is reported that the stripper cost $70,000, while the catalyst system cost $126,000. Catalyst life is expected to be 2

years with catalyst aging being the result of attrition of the catalyst pellets. Catalyst replacement cost has been quoted at $1,200. Performance data are not yet available (12).

The destruction performance achieved during pilot scale testing of an air stripper exhaust stream containing benzene and toluene is presented graphically in Figure 3 (13). The location of these tests was not identified. The incoming air from the stripping unit contained less than 10 ppmv total organics.

CASE STUDY 2: GRAPHIC ARTS

Dryer emissions from the graphic arts (heat set web offset printing) industry are primarily composed of hydrocarbon solvent, alcohol (if used), water vapor, and the byproducts of burner combustion (carbon dioxide and traces of unburned natural gas). Eventually all of these materials are exhausted from the dryer resulting in three pollution problems which need to be addressed: "smoke" or opacity, odor, and VOCs. The "smoke" observed is actually condensing ink solvents and water vapor. The odor is a function of the solvents and resins used. The organic compounds are the hydrocarbon solvents, alcohol, and unburned natural gas. A pollution control device must deal with all three of these problems to be effective.

Typical ink solvents used in the web offset industry are petroleum fractions distilled from crude oil and are similar to No. 2 fuel oil. These solvents typically boil in the range of 440 to 600 °F (225 to 315 °C) and are generally composed of approximately 85% aliphatic, 10% aromatic, and 5% olefinic hydrocarbons. Carbon numbers range from C_9 to approximately C_{20} with the largest concentration in the area of C_{14}. A typical molecular weight for these solvents is 210, and they typically have a net heating value of 19,950 Btu/lb (11,080 kcal/kg). The lower explosive limit (LEL) for a solvent of this type is approximately 0.455% by volume at 300 °F (150 °C)(14).

A second component of web offset dryer exhaust is often isopropyl alcohol. Used in the fountain solution, this very volatile material is carried with the web into the dryer where almost all is evaporated. It is very difficult to measure the amount of alcohol which does reach the dryer because a percentage of the alcohol escapes into the pressroom as fugitive emissions. Recent advances in the use of less volatile alcohol substitutes have greatly reduced the volume of alcohol used by printing plants.

One option for control of web offset emissions is catalytic incineration. Catalytic incinerators can be configured in the same manner as thermal incinerators with the use of primary heat exchangers to preheat the solvent-laden exhaust to the temperature necessary for catalytic oxidation. In addition, a secondary heat exchanger can be added as in Figure 1 to provide heated makeup air to the dryer.

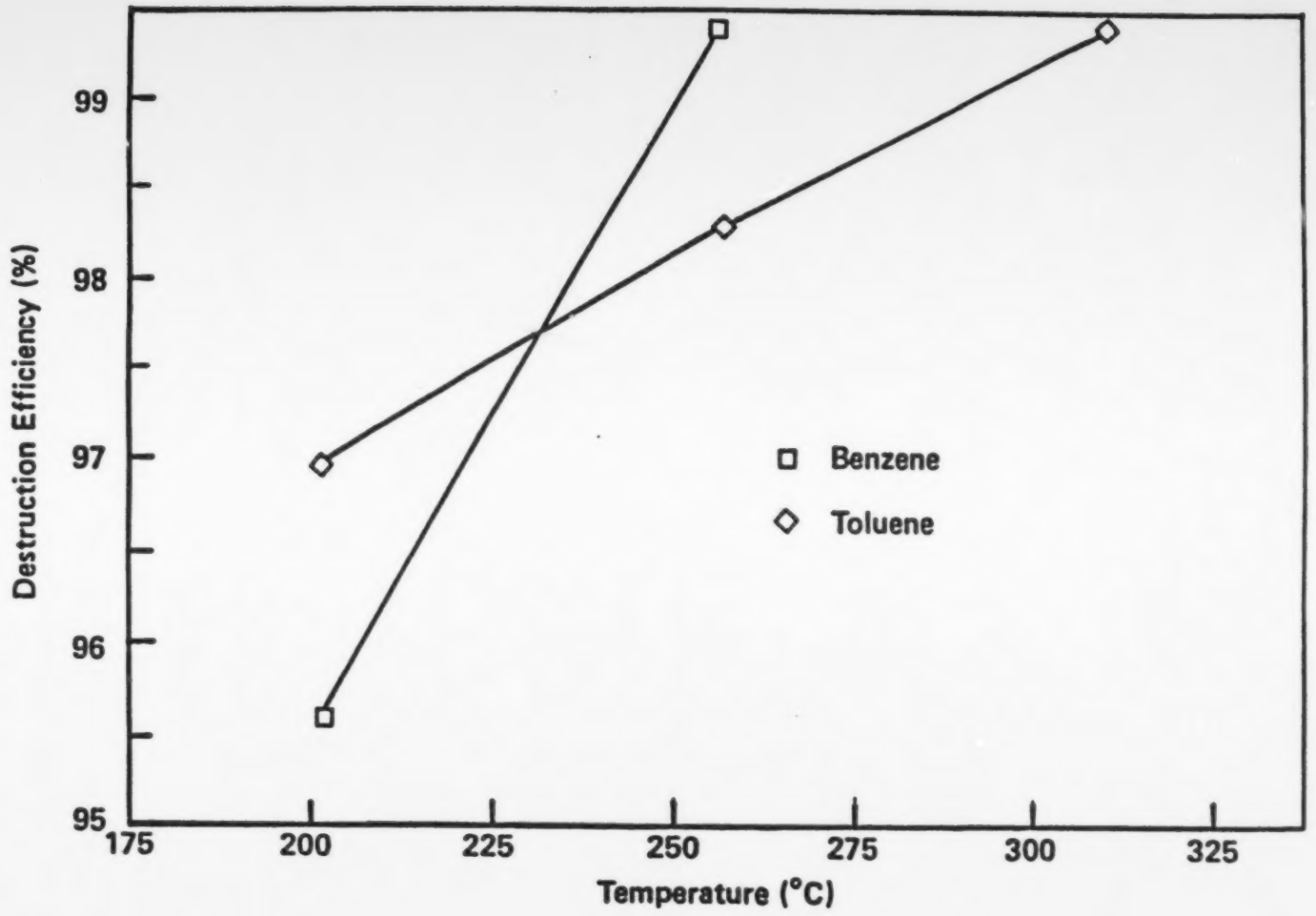


Figure 3. Destruction efficiency of a pilot scale catalytic incinerator for benzene and toluene in air stripper exhaust.

If, in the printing process, both the ink coverage is heavy enough and press speed is high enough, then the catalyst preheat burner may be able to shut off, allowing the unit to run with only the oxidation of ink solvent as a source of energy. This mode of operation presents the possibility for substantial energy savings. In addition, when heated makeup air is returned to the dryer, the need for fuel at the dryer is reduced. Alternatively, if the heated air is used to drive another recovery device (absorptive chiller, building heating and ventilating system, etc.), the auxiliary energy required to fuel that device would also be reduced.

Catalytic incineration does, however, suffer from a number of disadvantages in this application. Heat-up times are as long for catalytic units as for thermal units due to the large physical mass of catalyst which must be heated to the proper oxidation temperature. This disadvantage can be overcome to some extent. By incorporating an automatic damper, the system can be maintained in the "ready" mode with a minimum energy requirement. The cost of catalyst can be substantial causing the initial capital investment for a catalytic system to be from 15% to 30% higher than for an equivalent thermal system. Catalyst life may vary from 1 to 5 years or more depending on the composition of the catalyst, as well as operating and process variables (14).

In the graphic arts industry, the catalyst in catalytic incinerators should be monitored on a regular basis because it is susceptible to contamination by phosphorus (phosphate buffers) from fountain solutions, silica from silicone gloss-enhancer sprays, or chlorides from chlorinated solvents or blanket wash solutions. The precious metal catalyst is not poisoned by sulfur, but base metal catalysts are rapidly deactivated by sulfur in this type of application (15).

Phosphorus and silica accumulate most rapidly on the leading edge of the catalyst bed and deactivate the catalyst by masking the precious metals. Both phosphorus and silica bond to either the alumina substrate or alumina washcoat. Because of phosphorus and silica poisoning, TEC Systems, a major supplier to the printing industry of dryers and ancillary equipment including catalytic incinerators, has gone to bead type catalyst beds with low space velocities (about 7,000 to 8,000 GHSV) (15). With deeper catalyst beds, the leading edge of the catalyst tends to collect the poisons and thus protects the catalyst beads deeper in the bed. Catalyst beds with high space velocities (near 30,000 GHSV), such as monolith catalysts, often require frequent cleaning, sometimes as often as every 3 months.

Chloride poisoning is much less common than phosphorus or silica poisoning; however, since it reacts directly with the precious metals, chloride deactivates the catalyst at much lower concentrations. Three potential sources of chloride poisoning are fire extinguishing systems, refrigeration systems which utilize fluorocarbons such as trichlorotrifluoroethane, and chlorinated hydrocarbon solvents (15).

In some cases, TEC Systems has found that a catalyst unit may fail a compliance test even though the catalyst is in good shape (15). Failures of

this nature have been traced to cracked heat exchangers, low catalyst levels, abnormally low incineration temperatures, leaking bypass dampers, and erroneous testing.

CASE HISTORY 3: FLEXOGRAPHIC PRINTING PLANT

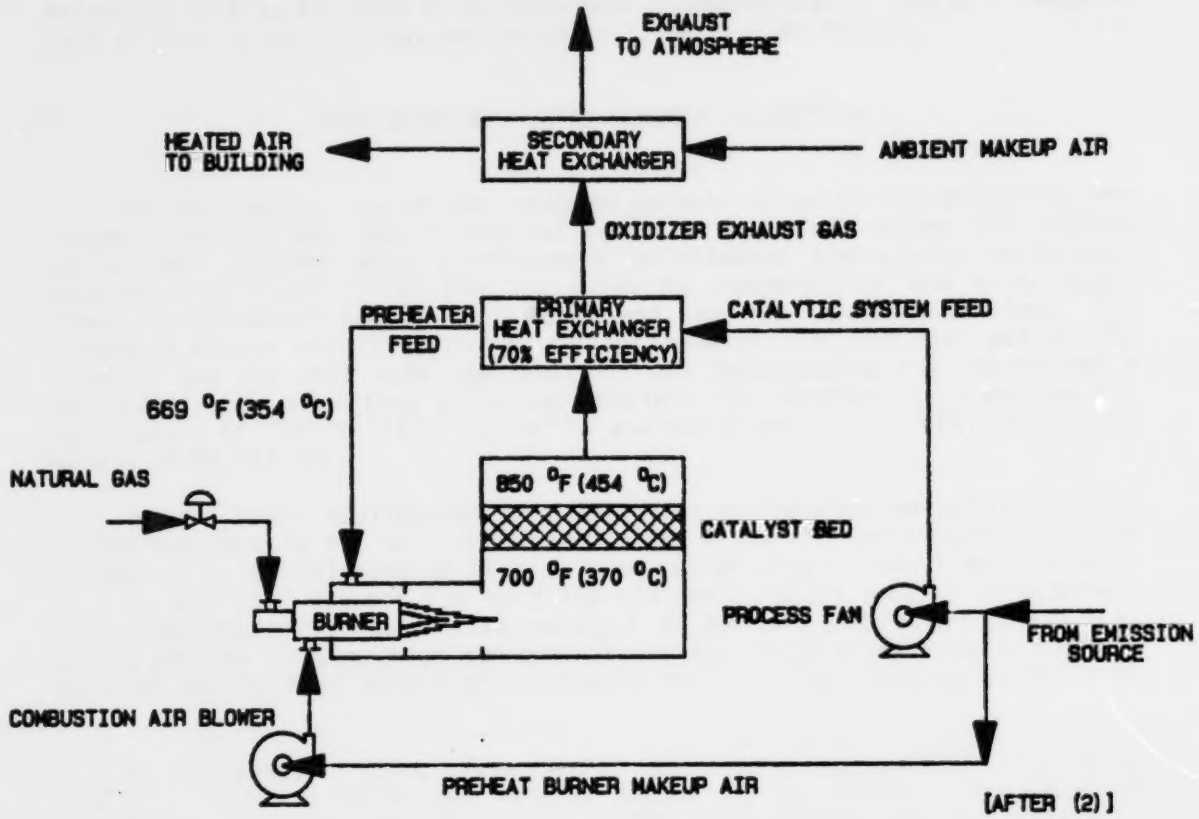
A metal oxide catalyst in a fluidized bed configuration has been applied to a flexographic printing plant in Massachusetts (2). In many ways, this use is similar to the graphic arts application discussed in Case 2. The exhaust fumes from 10 flexographic printing drying ovens containing 120 lb/hr (55 kg/hr) of VOC, 5 lb/hr (2.3 kg/hr) of silicones, and trace amounts of chlorinated hydrocarbons are controlled using catalytic oxidation. However, since the catalyst surface is continually renewed by abrasion in the fluidized bed, the problem of masking the catalyst surface with silicones is avoided. The use of a metal oxide catalyst avoids the problem of chlorine poisoning. Massachusetts' environmental emission regulations require at least 95% capture or destruction.

The system was installed in October 1986. Operating conditions are shown in Table 3, and are typical of those used for easily combusted emissions. The vendor states that the tested efficiency was in excess of 99%. This high destruction efficiency is attributed to operation at 73% of design air flow rate. Decreased flow (hence decreased space velocity) increases destruction efficiency. The plant operates 24 hrs/day, 5 days/wk, and 260 days/yr. The incineration system also includes a 70% thermally efficient self-recuperative plate type heat exchanger for building heating. Design conditions are shown on the flow sketch of Figure 4.

Table 3. Operating Conditions for Catalytic Control of a Flexographic Printing Plant (2)

Air Flow Rate	11,000 scfm	18,700 Nm^3/hr
(Design Value)	15,000 scfm	25,500 Nm^3/hr
VOC Loading	3 to 6 % of LEL	
(Fuel Value)	1.5 to 3.1 Btu/scf	13 to 28 kcal/Nm^3
Bed Inlet Temperature	700 °F	370 °C
Bed Outlet Temperature	775 to 850 °F	415 to 455 °C
Catalyst Pressure Drop	10 in. water	18.7 mm Hg
Fuel Consumption	0.451 x10^6Btu/hr	114,000 kcal/hr

The cost of the catalytic incinerator including the catalyst and process fan but not including the cost of heat exchangers was $133,430. The annual operating cost for fuel is $14,071/yr at an energy cost of $5.00/$10^6$Btu ($0.00002/kcal). This value does not include any credit for building heating costs which were cut by 50%. Catalyst costs are $5,377/yr.



NATURAL GAS FUEL

1,010 Btu/scf	(8,990 kcal/Nm^3)
2 psig	(14 kPa)
10.14 scfm	(17.23 Nm^3/hr)
0.615×10^6 Btu/hr	(155,000 kcal/hr)

PROCESS FAN & SYSTEM FEED

15,000 scfm	(25,485 Nm^3)
17,972 acfm	(30,530 m^3)
175 °F	(79 °C)
3.1 Btu/scf	(27.6 kcal/Nm^3)

COMBUSTION AIR BLOWER

688 scfm	(1,169 Nm^3/hr)
840 acfm	(1,427 m^3/hr)
175 °F	(79 °C)

OXIDIZER EXHAUST GAS

15,010 scfm	(25,500 Nm^3)
24,160 acfm	(41,050 m^3)
377 °F	(192 °C)

Figure 4. Catalytic oxidation system - typical operating conditions.

The vendor also calculated costs for a thermal incinerator operating at 11,000 scfm (18,700 Nm^3/hr) with the same heat recovery. Fuel costs were estimated at \$159,931/year at \$5.00/10^6Btu (\$0.00002/kcal). The exit temperature of the incinerator was estimated as 1,400 °F (760 °C)(2).

CASE STUDY 4: LATEX MONOMER PRODUCTION

For many years, one of the accepted methods of oxidizing gaseous hydrocarbon emissions has been by thermal incineration. This became the obvious choice when dealing with carcinogenic chlorinated hydrocarbon emissions; however, with 2,200 °F (1,200 °C) oxidation temperatures and 2-sec dwell times, incinerators became very large and the fuel costs excessive. The alternate choice was catalytic oxidation; however, the catalyst was easily poisoned and the unit made ineffective. ARI Technologies has introduced a catalyst system which they claim can complete the reaction at an average bed temperature of 700 °F (370 °C) while achieving conversion efficiencies in excess of 99.99% (2).

One difficult application of chlorinated hydrocarbon emissions control is the manufacture of latex monomers. Being a typical batch operation, the concentration of chlorinated hydrocarbons varies widely from a heat content of 4 to over 300 Btu/scf (36 to 2,700 kcal/Nm^3), which results in a potential temperature rise across the catalyst of 200 to 1,500 °F (95 to 815 °C). During periods of very high concentrations, the temperature rise across the catalyst bed is kept within a reasonable range by the addition of dilution air.

At the present time, five plants are operating successfully using catalytic incineration as the control technology of choice. The range of operating parameters for a typical 4,000 scfm (6,800 Nm^3/hr) catalytic incineration system is shown in Table 4. Note the wide range of dilution air rates needed to compensate for the heat content of the process gas and the need for caustic scrubbing for control of hydrochloric acid (HCl) emissions. The high conversion efficiency may be possible, if the chlorinated hydrocarbon is vinyl chloride, based on laboratory results which seem to indicate that vinyl chloride combustion goes to completion below 700 °F (370 °C)(16).

Table 4. Operating Conditions for Catalytic Control of Latex Monomer Production Emissions (2)

Chlorinated HC Gas Flow	50 to 335 scfm	85 to 570 Nm^3/hr
Inlet Temperature	700 °F	370 °C
Heat Content	4.4 to 225 Btu/scf	39 to 2,000 kcal/Nm^3
Fuel Gas Consumption	0.9 to 3.0 scfm	1.5 to 5.1 Nm^3/hr
Dilution Air Flow	60 to 3,000 scfm	100 to 5,100 Nm^3/hr
Cooling Water Rate	110 to 1,000 gph	415 to 3,800 l/hr
Caustic Addition Rate	0 to 150 gph	0 to 570 l/hr
Water & Caustic to Drain	65 to 750 gph	250 to 2,850 l/hr
Stack Temperature	95 to 160 °F	35 to 70 °C
Conversion Efficiency	99.999%	

The cost of a typical 4,000 scfm (6,800 Nm^3/hr) system including the major items of equipment shown in Figure 4, water and caustic manifolds, controls and control panel, catalyst and service platforms is $350,000 to $400,000. The unit, which is preassembled during fabrication, can be installed in the field in approximately 7 days at an assembly cost of approximately $25,000. The operating costs of the system are a function of the chlorinated hydrocarbon concentrations and the individual plant operating procedure and can only be calculated based on a specific application (2).

CATALYTIC UNITS FOR CONTAMINANT REMOVAL

There are several commercial catalytic units now on the market in this country, and many others in Europe. However, to our knowledge, there is experience with only three of these in conjunction with an air stripping unit. Most of these units are now used for controlling emissions from solvent stripping operations, paint spray booths, and similar industrial operations where concentrations of reactants are much higher than air stripping emissions. Several of the commercially available catalytic incinerators have been identified and are described below:

1. ARI: This fluidized bed catalytic incinerator was developed in the early 1970s. Developed jointly by Air Resources, Inc. (ARI) and Harshaw Chemical Company, this technology has been in commercial use since 1975 and is being marketed on a turnkey basis (16). The catalyst is a nonprecious metal disposable pellet. The fluidized design is especially good in that it overcomes carbon fouling (masking) problems. The moving catalyst bed allows masked catalyst to move to higher temperature zones in the bed, thereby oxidizing the masking material. Other mineral deposits (e.g, sulfur, phosphorus, silicon, salts) which may coat the surface are removed from the catalyst pellet by attrition in the fluidized bed. This results in a catalyst life of about 2 years.

Approximately 50 of these fluidized bed units are being used for VOC control. Of the 50, a significant portion are used for control of chlorinated hydrocarbons.

ARI and Union Carbide have recently cooperated to develop a new system employing ARI fluidized bed catalyst technology and Union Carbide molecular sieve adsorbent expertise. Their system uses Silicalite adsorbent to preconcentrate organic emissions before they are fed to the catalytic unit. The combined system is said to be more cost effective than catalytic destruction alone since the catalytic unit can be downscaled by a factor of 10 or more (2).

2. CE Air Preheater: CE markets both thermal and catalytic incinerator systems in sizes ranging from 2,000 to over 100,000 scfm (3,400 to 170,000 Nm^3/hr). Their catalyst, supplied by Johnson-Matthey, is platinum deposited on a stainless steel honeycomb. CE Air Preheater has installed 17 catalytic incinerator systems as of 1988 (17).

3. Dedert Corporation: Dedert markets a "CATOX" catalytic incinerator for Haldor Topsoe A/S, a Danish company specializing in catalysts. It features a non-noble metal catalyst resistant to chlorine, sulfur, and phosphorus compounds in both monolithic and pelleted forms. They market a special "ADOX" unit for low concentrations (less than 250 ppmv), and another, named "REGENOX," for "dirty" streams. Many of these units are in place for manufacturing and industrial processes.

4. Engelhard (Torvex): Since the early 1980s, this system has been marketed by the Engelhard Corporation. Complete systems are available in sizes ranging from less than 1,000 to 70,500 scfm (1,700 to 120,000 Nm^3/hr). Their catalysts consist of precious metal deposited on ceramic honeycombs. Between 1976 and 1988, the vendor supplied about 250 complete catalytic incinerator systems in the U.S. and over 1,000 in Japan and has retrofitted about 200 thermal incinerators with catalyst.

5. Groundwater Technology, Inc.: Groundwater Technology provides complete groundwater cleanup services. As such, they have entered the area of cleanup of air emissions from these operations. They report installation of their first catalytic conversion unit. The catalyst was obtained from Johnson-Matthey and consists of platinum on a metal substrate. Effective destruction of fuel mixtures stripped from groundwater has been cited (13).

6. Johnson-Matthey: A major manufacturer of catalysts and other materials employing precious metals markets a variety of self contained catalyst treatment systems for removal of organic compounds from gaseous emissions. Their "Honeycat" unit may be fitted with either a ceramic or metal honeycomb catalyst support. Inexpensive units are marketed for treatment of low volume streams.

7. Met-Pro Corporation: Formerly Oxy-Catalyst, this company markets both thermal and catalytic incineration systems and carbon adsorption systems. They employ a wide range of catalysts including both precious and non-precious metals deposited on a monolithic or pelleted support. They have installed over 200 catalytic incinerator systems throughout the United States and some foreign countries (18).

8. TEC Systems: This subsidiary of W.R. Grace manufactures and markets catalytic incinerator systems that utilize both granular and monolithic noble metal catalysts on alumina substrates. Their granular catalyst is manufactured by Davison. These incinerators have been effectively used to control VOC emissions from a number of industrial processes, primarily in the printing industry (15).

9. Ultrox: Ultrox International continues to develop and market a system based on a combined ultraviolet (UV)/ozone/catalytic oxidation technology. When used for water treatment, the groundwater contaminated with chlorinated hydrocarbons is pumped into a reaction tank where an ozone/air mixture is bubbled through the water. This bath is simultaneously irradiated with UV light. In addition to the oxidation in the aqueous phase, a portion of the hydrocarbons are stripped from the water and pass into a UV catalytic reactor where further oxidation occurs at temperatures slightly above ambient.

In general, a catalyst with high activity at low temperatures is desirable, but enough heat must be supplied to effect complete destruction. However, extremely high temperatures [greater than 1,380 °F (750 °C)] may actually produce additional partial reaction products. Basically, this means that a minimum operating temperature of at least 660 °F (350 °C) should be employed with currently available catalysts. Most catalyst units, regardless of the catalyst bed structure, use a preheating unit to attain these temperatures. This preheater may be electric or an open flame type. The open flame type is generally powered by natural gas or propane, and may accomplish a significant degree of destruction by itself (10). These preheaters are used with most of the reactors now available commercially, in both fixed and fluidized bed designs.

ECONOMICS

The Control Technology Center (CTC) report summarizes control costs and efficiencies for carbon adsorption at four air stripper sites (11). It then completes estimates of control costs at these sites for thermal incineration and catalytic oxidation at 98% and 95% efficiency, respectively.

Table 5 summarizes these estimates. It may be noticed from this table that the annualized costs of control increase as a function of air flow rate for all of the systems. The most rapid increase in cost is for thermal incineration, with catalytic oxidation being twice as cost effective for the 19,200 scfm (32,600 Nm^3/hr) unit. This emphasizes the energy savings mentioned previously for catalytic systems. Carbon adsorption still has a more favorable operating cost; however, for the operating systems considered in the CTC report, the expected control efficiencies for thermal and catalytic incineration (more than 95%) were much greater than the observed efficiencies for adsorption (70 to 90%). Of course, carbon adsorption can attain higher control efficiencies with increased bed size or decreased relative humidity of the emission stream. However, such changes will result in increased capital and annualized operating costs. A cost analysis for an existing high efficiency (greater than 95%) carbon adsorption system is not presently available. The tradeoffs between control efficiency and costs must be made in light of the seriousness of the contamination threat.

Table 5. Summary of Air Stripping Exhaust Control Systems (11)

	Site A	Site B	Verona Well field	Plainfield
Contaminants Concentration (ppbw)	Trichloroethylene (4,000) Trichloroethane (300)	Chloroform (1,500)	Ethylene dichloride (5) Trichloroethane (12) Dichloroethylene (10) Trichloroethylene (1) Perchloroethylene (10)	Perchloroethylene (200)
Water Flowrate (gpm)*	1.400	155	1.900	3.600
Air Flowrate (scfm)#	8.000	1.300	5.500	19.200
Removal efficiency (%)	99	99.9	99.9	99.6
Control Options:				
Carbon Adsorption				
Control efficiency (%)	~80	not reported	74	90
Installed cost ($)	150.000	152.000	223.000	500.000
Direct operating cost ($)	50.400	31.300	62.700	120.000
Total annualized costs ($)	96.400	77.800	124.000	221.400
Thermal Incineration				
Control efficiency (%)	98	98	98	98
Installed cost ($)	318.000	187.000	285.000	432.000
Direct operating cost ($)	432.000	86.800	303.000	1.047.000
Total annualized costs ($)	492.000	129.000	358.000	1.123.000
Catalytic oxidation				
Control efficiency (%)	95	95	95	95
Installed cost ($)	307.000	135.000	251.000	586.000
Direct operating cost ($)	210.000	51.600	150.000	508.000
Total annualized costs ($)	269.000	86.100	201.000	606.000

* 1 gpm = 3.785 liter/minute # 1 scfm = 1.699 Nm^3/hr

SUMMARY AND CONCLUSIONS

Catalytic oxidation is an air pollution control technique whereby VOCs and gas-phase organic air toxics are oxidized at destruction efficiencies of greater than 95%. The presence of the catalyst accelerates the rate of oxidation at a given temperature. This allows combustion at lower temperatures than are possible in thermal incinerators. Catalysts can be either noble or non-noble metals deposited on either pelleted or monolithic supports composed of either ceramic or metal. Fixed and fluidized bed catalyst systems are available. The most important factors affecting performance are operating temperature, space velocity (reciprocal of residence time), contaminant concentration and composition, catalyst properties, and the presence of catalyst poisons or inhibitors in the emissions stream. The economics of catalytic oxidation can generally be enhanced by the use of primary heat recovery to supplement and sometimes replace electric or gas preheating of the emissions stream before it is fed to the catalyst bed. Secondary heat recovery for other process uses can also improve system economics.

Catalytic technology has had limited application to the control of groundwater stripping emissions in the field. The known barriers to its application are the dilute nature of air emissions from strippers, the high humidity content of the air stream, the complex chemical nature of the emissions, the need to control chlorinated compounds, and the presence of catalyst poisons and inhibitors such as hydrogen sulfide, biological organic matter, and mineral salts. Limited data from the three known installations are available.

The printing and graphic arts industries make great use of catalytic oxidation for control of their air emissions. Two applications of catalytic technology are discussed. In both cases, the vendor claims high destruction efficiency (greater than 95%) at moderate inlet temperatures [700 °F (370 °C)] due to the ease of combusting the emissions. Both vendors identify the presence of phosphorus, silicon, sulfur, and halogens in the exhaust stream as potential inhibitors of catalyst effectiveness. The supplier of the granular fixed bed noble metal on alumina catalyst system is concerned primarily about masking from phosphorus and silicon, and about deactivation from the halogens. The supplier of the fluidized bed non-noble metal oxide catalyst recognizes the potential for masking, but is not concerned since the surface of their catalyst pellet is believed to be continually cleaned in the fluidized bed. In addition, they are apparently not concerned about the deactivation of non-noble metal catalysts by halogens. Several causes of low destruction efficiency other than catalyst deactivation are identified: low operating temperatures and catalyst levels, and the bypassing of the catalytic unit via cracked heat exchangers and leaking bypass dampers.

One vendor has provided information about the use of a fluidized bed metal oxide catalyst system for destruction of chlorinated hydrocarbon emissions at five sites. They claim a very high destruction efficiency (greater than 99%) at moderate temperatures [700 °F (370 °C)]. Of particular interest in this application is the high variability of organic emission rates and the need to add dilution air to the emission stream to avoid overheating of the catalyst bed. The need for scrubbing of hydrochloric acid (HCl)from the catalytic incinerator exhaust is also of note.

Nine catalyst systems for contaminant removal have been identified. Most of these units are now used for controlling emissions from solvent stripping operations, paint spray booths, and similar industrial operations where the concentration of reactants range from 250 to 1,500 ppmv or higher as limited by 25% of the lower explosive limit (LEL). Both noble metal catalyts and non-noble metal oxide catalysts are represented. These use both pelleted ceramic and monolithic (honeycomb) ceramic or metal supports. Pelleted catalysts are in use in both fixed and fluidized beds.

Finally, the economics of three control technologies are evaluated for groundwater stripping gaseous emissions. Existing data for carbon adsorption applications are compared to estimates for the combustion technologies. Carbon adsorption has a more favorable annualized cost; however, the expected control efficiencies for thermal and catalytic incineration (higher than 95%) were much greater than the observed efficiencies for adsorption (70 to 90%). Cost analyses for an existing high efficiency carbon adsorption system are not presently available.

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